

## Internal Degrees of Freedom and Anelasticity in Glasses

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### *Abstract*

An extension of the AHV–Phillips model is proposed which describes the anelastic and time-dependent behaviour of glasses over a range of temperatures. The model assumes the existence of groups of atoms with two or more metastable locations in the matrix. Transitions between these locations are assumed to be thermally activated, and the parameters of the potential seen by such groups are assumed to be continuously distributed. The active groups are a realization of internal degrees of freedom in the sense of irreversible thermodynamics. The thermodynamic description is particularly convenient when strain couplings are involved, since Maxwell relations determine the internal contribution to the stress in terms of the strain dependence of the internal potentials. Several consequences of the model, such as time-dependent heat capacities, time-varying stress–strain relations etc., are investigated and found to be consistent with existing experiments. In particular, Wiedmann’s elastic after-effect measurements of 1886 can be fitted and lead to values of 0.6–0.9 eV for the width of the distribution of energy barriers. However, the predicted ultrasonic attenuation from active groups conflicts with experiment, and reasons for this are discussed.

### 1. Introduction

The intrinsic low temperature properties of glasses are tolerably well understood in terms of the model proposed by Anderson *et al.* (1972) and independently by Phillips (1972); hereinafter referred to as the AHV–Phillips model. Many experiments have been performed below 10 K (references may be found in the review articles by Halperin 1976 and Black 1978) and much of this work can be accommodated within the AHV–Phillips model. However, no time dependence comparable with predictions of the theory has been observed in the specific heat (Goubau and Tait 1975; Kummer *et al.* 1978); it is not clear if this is a shortcoming of the model itself or of existing treatments of it.

There exists a much older body of experimental work, usually carried out at room temperature or above, which establishes the unique properties of glasses and sets them apart from conventional solids and liquids. The most well-known effect is ‘creep’, i.e. flow under stress. The conventional folklore is that glasses are super-cooled liquids and therefore slow viscous flow, or creep, is to be expected. However, quantitative observations (mostly rather ancient ones) show that the observed creep is not described by Newtonian viscous forces but by time-dependent stress–strain relations, in many cases with a logarithmic time dependence. This so-called anelastic behaviour (Zener 1948) can be shown to result from internal relaxation of stress, in which case an  $\ln t$  behaviour arises from a very wide distribution (many octaves) of

relaxation times. A very similar picture was proposed many years ago by Néel (1949) for the relaxation of superparamagnetic particles. Another well-known phenomenon unique to glasses is the so-called 'secular rise of the zero' in glass thermometers, caused by thermal creep of the glass tube following cooling after the manufacturing process. This effect is firm evidence for the existence of thermally induced internal processes.

Our model is basically the AHV-Phillips model except that transitions between potential minima take place by thermal activation rather than tunnelling. Specifically, we assume that every glass contains a certain number  $N$  of active atoms or groups of atoms which can exist in either of two adjacent minima in the local potential surface. The restriction to two minima only is convenient but not essential. The number  $N$  is some finite fraction of the total number of atoms in the glass; this fraction is presumed to be small so that interactions between active groups can be neglected. At low temperatures the active groups should be identified with those of the AHV-Phillips model, so that at sufficiently low temperatures tunnelling will take over from thermal activation as the dominant mechanism for transitions. At high temperatures the potential of each active group must be temperature dependent, becoming free of minima at temperatures near the glass transition. The usefulness of our theory could be extended if the temperature dependences of the potentials were known, e.g. from some kind of mean field approximation. As this information is not available, we assume that each potential is fixed, and therefore the theory is restricted to temperatures well below the glass temperature.

In the next section the basic properties of the model are specified using irreversible thermodynamics. These are applied to time-dependent heat capacities in Section 3, anelasticity in Section 4, thermal creep in Section 5 and finally dispersion and damping of ultrasonic waves in Section 6. Other phenomena such as thermal conductivity require explicit reference to the phonon bath and will not be considered here.

## 2. Irreversible Thermodynamics of Internal Degrees of Freedom

The description of internal degrees of freedom in irreversible thermodynamics was given by Prigogine and Mazur (1953), Meixner (1957) and also de Groot and Mazur (1962). The basic assumption is that for each active group there is a set of  $d$  internal coordinates  $q_i$ ,  $i = 1, \dots, d$ , which specify internal motions through an appropriate potential  $V(\mathbf{q})$ . The space of internal coordinates is orthogonal to the normal or external coordinate space specifying the motions of the matrix. The nature of the internal coordinates is clear enough in the case of molecular degrees of freedom (rotations and vibrations) but is slightly obscure for glasses. In what follows, we assume that  $d = 1$ .

Internal degrees of freedom are accommodated within thermodynamics by regarding internal motions as chemical reactions. The internal position  $q$  of a group thus becomes a chemical label and the transition from  $q$  to  $q + dq$  becomes a unimolecular chemical reaction. The basic expression for the rate of irreversible entropy ( $S_{ir}$ ) production is thus

$$\dot{S}_{ir} = -T^{-1} \sum_{\alpha} \int dq A^{(\alpha)}(q) \dot{\xi}^{(\alpha)}(q), \quad (1)$$

where  $A^{(\alpha)}(q)$  is the chemical affinity of the reaction  $q \rightarrow q + dq$ ,  $\xi^{(\alpha)}(q)$  is the degree of advancement of the reaction which increases by unity for each reaction proceeding

from left to right, and  $\alpha$  labels active groups of different kinds. Let  $N^{(\alpha)}(q)$  be the number density in  $q$  space of active groups of type  $\alpha$  at some instant in time,  $I^{(\alpha)}(q)$  the corresponding flux and  $\mu^{(\alpha)}(q)$  the chemical potential. Then it follows from the definitions of affinity etc. that

$$A^{(\alpha)}(q) = \partial \tilde{\mu}^{(\alpha)}(q) / \partial q, \quad \xi^{(\alpha)}(q) = I^{(\alpha)}(q), \quad (2)$$

where

$$\tilde{\mu}^{(\alpha)}(q) = \mu^{(\alpha)}(q) + V^{(\alpha)}(q) \quad (3)$$

is the chemical potential in the presence of the potential  $V^{(\alpha)}$ . With the continuity equation

$$\dot{N}^{(\alpha)}(q, t) + \partial I^{(\alpha)}(q, t) / \partial q = 0, \quad (4)$$

these relations enable equation (1) to be rewritten in the form

$$\dot{S}_{\text{ir}} = -T^{-1} \sum_{\alpha} \int dq I^{(\alpha)}(q, t) \partial \tilde{\mu}^{(\alpha)}(q, t) / \partial q, \quad (5)$$

which is more useful for our purposes.

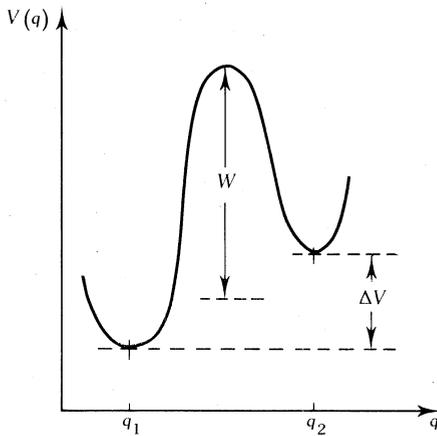


Fig. 1. Illustrating the characteristic parameters of the double-well potential seen by an active group.

Note that the potential  $V^{(\alpha)}$  in equation (3) is to be regarded as a fixed or external potential in the context of the model. Thus the condition for internal equilibrium of an active group is that  $\tilde{\mu}^{(\alpha)}$  be independent of  $q$ . On treating the active groups as independent particles, we obtain their chemical potential in the form

$$\mu^{(\alpha)}(q) = k_B T \ln N^{(\alpha)}(q) + \text{const.} \quad (6)$$

This means that the equilibrium distribution in  $q$  space is a Boltzmann distribution, proportional to  $\exp(-V^{(\alpha)}/k_B T)$ . It is curious that a purely thermodynamic theory can predict the full equilibrium distribution, and hence fluctuations, but the device of treating phase-space coordinates as chemical labels has been used by Woods (1975) in a systematic derivation of the kinetic theory of gases.

The model is completely specified by assuming a particular response function for nonequilibrium flow in  $q$  space. We assume that the flow is linear in the affinity, and that affinities and fluxes of different  $q$ 's do not couple (Prigogine and Mazur

1953). The first assumption is not as drastic as it appears, since it allows arbitrarily large deviations from equilibrium for the populations of each well of the potential. The second assumption implies that motion along the  $q$  coordinate proceeds continuously rather than by large jumps, analogously to Brownian motion. The motion is then described, as might be expected, by a Fokker-Planck equation. Its coefficients will be constants if the original Onsager coefficient is chosen linear in  $N^{(\alpha)}(q)$ , that is,

$$I^{(\alpha)}(q) = U N^{(\alpha)}(q) \left( -\frac{\partial \tilde{\mu}^{(\alpha)}(q)}{\partial q} \right) = U N^{(\alpha)}(q) \left( -\frac{\partial V^{(\alpha)}}{\partial q} - D \frac{\partial N^{(\alpha)}(q)}{\partial q} \right), \quad (7)$$

where  $U$  is a mobility, assumed constant for all groups,  $D$  is a diffusion coefficient and Einstein's relation  $D = k_B T U$  is satisfied automatically.

The general form of the potential is indicated in Fig. 1, with an average barrier height  $W^{(\alpha)}$  and a difference  $\Delta V^{(\alpha)}$  between the two minima. For the active groups that contribute to slow time-varying responses, the barrier heights will be larger than  $k_B T$  and hence the active groups will nearly all be found in one or the other potential minimum. This suggests working with the populations in each potential well rather than with the entire distribution  $N^{(\alpha)}(q)$ . Let  $n_1^{(\alpha)}$  be the number of groups in the lower potential well, the well being loosely defined as a region around a minimum in which the potential rises by several times  $k_B T$ . This is sufficient to define  $n_1$  quite precisely (Brown 1963). As the distribution within each well will be Boltzmannian over the time scale of interest, we have

$$n_1^{(\alpha)} = N^{(\alpha)}(q_1) \int \frac{N^{(\alpha)}(q)}{N^{(\alpha)}(q_1)} dq = N^{(\alpha)}(q_1) \exp(S_1^{(\alpha)} k_B), \quad (8)$$

which defines  $S_1^{(\alpha)}$ , the entropy associated with motion inside the well. Because the population between wells is negligible, the population  $n_2^{(\alpha)}$  in well 2 will almost be equal to  $N^{(\alpha)} - n_1^{(\alpha)}$  and steady state conditions will prevail, that is,  $I^{(\alpha)}(q)$  will be independent of  $q$ . This leads to much simpler forms of the basic results; the rate of entropy production is now

$$\dot{S}_{\text{ir}} = -T^{-1} \sum_{\alpha} I^{(\alpha)} \Delta \tilde{\mu}^{(\alpha)}, \quad (9)$$

where

$$\Delta \tilde{\mu}^{(\alpha)} = \tilde{\mu}^{(\alpha)}(q_2) - \tilde{\mu}^{(\alpha)}(q_1) = k_B T \ln(n_2^{(\alpha)}/n_1^{(\alpha)}) + \Delta F^{(\alpha)} \quad (10)$$

with

$$\Delta F^{(\alpha)} = \Delta V^{(\alpha)} - T \Delta S^{(\alpha)} \quad (11)$$

the difference of the free energies between wells. Furthermore, under steady state conditions the Fokker-Planck equation can be solved for the distribution function. This solution enables the flux to be expressed in terms of the well populations. Thus by continuity we have

$$\dot{n}_1^{(\alpha)} = -I^{(\alpha)} \quad (12)$$

and

$$I^{(\alpha)} = W_{12}^{(\alpha)} n_1^{(\alpha)} - W_{21}^{(\alpha)} n_2^{(\alpha)}, \quad (13)$$

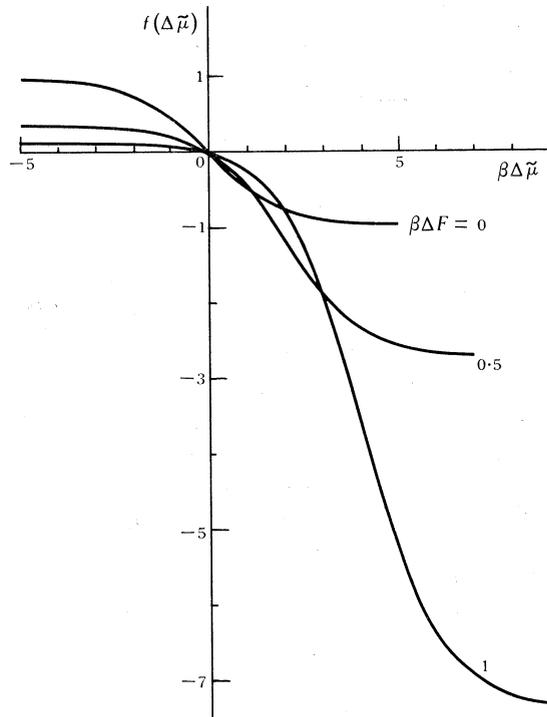
where

$$W_{12}^{(\alpha)} = \frac{D \exp(\beta F_1^{(\alpha)})}{\int_{q_1}^{q_2} \exp(\beta V^{(\alpha)}) dq}, \quad W_{21}^{(\alpha)} = \frac{D \exp(\beta F_2^{(\alpha)})}{\int_{q_1}^{q_2} \exp(\beta V^{(\alpha)}) dq} \quad (14)$$

and  $\beta = 1/k_B T$ . Detailed balancing is satisfied as the equilibrium population is proportional to  $\exp(-\beta F)$ , free energy  $F$  replacing potential energy  $V$  to allow for internal motions within the well. It is interesting to interpret the flux over the potential barrier as being driven by the difference  $\Delta\tilde{\mu}$  of the modified chemical potentials. The flux response is proportional to  $f(\Delta\tilde{\mu})$ , where

$$f(\Delta\tilde{\mu}) = [1 - \exp(\beta \Delta\tilde{\mu})] / [\exp(\frac{1}{2}\beta \Delta F) + \exp\{\beta(\Delta\tilde{\mu} - \frac{1}{2}\Delta F)\}]. \quad (15)$$

This function is zero in equilibrium where  $\Delta\tilde{\mu} = 0$ , is linear for  $\Delta\tilde{\mu} \ll k_B T$  and saturates at different levels for large positive and negative driving forces, where the populations are all driven into one well (see Fig. 2). The asymmetry of this response is due to the difference in free energies between each well. However, the original flux in  $q$  space was assumed to be linear in the affinity; by working instead with the well populations one goes from linear to highly nonlinear response.



**Fig. 2.** Flux response function  $f$ , defined by equation (15), plotted as a function of the modified chemical potential difference  $\Delta\tilde{\mu}$  between wells for the three indicated values of the free energy difference  $\Delta F$ .

Nothing has yet been said about the variations of potential amongst the active groups. Fortunately, one does not need the distribution function for the whole potential, but only for those parameters which appear in the theory, namely  $W$  and  $\Delta F$  so far. It is sufficient to regard  $\alpha$  as a label specifying values of  $W$  and  $\Delta F$ , plus any other potential parameters that may occur, so that  $N^{(\alpha)}$  is to be replaced by  $N(W, \Delta F, X_1, X_2, \dots) dW d\Delta F dX_1 dX_2 \dots$ , the number of active groups with parameter

values in the ranges  $W$  to  $W+dW$ , etc. The simplest assumptions to make about this joint distribution are that:

- (i) the variables  $W$ ,  $\Delta F$ ,  $X_1$ ,  $X_2$ , ... are uncorrelated, and
- (ii) the separate distributions of  $W$  and  $\Delta F$  are flat on an energy scale of  $k_B T$ .

In fact, one has very little idea of the characteristic energy scale of these two distributions, except that in either case the scale energy is almost certainly larger than thermal energies. Experience with the AHV-Phillips model at low temperatures tends to confirm the assumption (ii). Other parameters ( $X_1$ ,  $X_2$ , ...) should be considered individually.

### 3. Time-dependent Heat Capacities

One of the simplest predictions of the model is that there is a time-dependent contribution to the heat capacity, whether at constant volume or pressure, proportional to  $T^2$  and also to  $\ln t$  in a certain time domain. It arises from delayed thermalization of active groups, as described by Anderson *et al.* (1972) and Phillips (1972), except that an extra power of temperature appears in the number of groups which equilibrate in times less than  $t$ . A crude derivation proceeds as follows.

Equations (13) and (14) show that the well population  $n$  relaxes exponentially to equilibrium with a relaxation time  $\tau(W, \Delta F)$  given by

$$\tau^{-1} = f \cosh(\frac{1}{2}\beta \Delta F) \exp(-\beta W), \quad (16)$$

where  $f$  is a temperature-dependent constant. As noted in the Introduction,  $\tau$  will vary over many octaves for one octave of variation in  $W$  provided that  $\beta W$  is mostly larger than unity, which is expected anyway. Hence the vast majority of active groups will either have  $\tau \ll t$ , in which case they will equilibrate very rapidly, or  $\tau \gg t$ , for which they will remain frozen in their initial wells. This suggests an approximation used to great effect by Néel (1949) in superparamagnetic particle theory: assume all active groups either come to equilibrium instantly or not at all. The error involved in Néel's approximation is the fraction of groups with relaxation times within one octave (say) of  $t$ , which is of order  $k_B T/W_0$  where  $W_0$  is the width of the distribution of barrier heights. The contribution of active groups to the heat capacity  $C$  is then

$$\Delta C(t) = \iint_{\tau(W, \Delta F) < t} dW d\Delta F \frac{\Delta V \Delta F}{4k_B T^2} \operatorname{sech}^2\left(\frac{\Delta F}{2k_B T}\right) N(W, \Delta F). \quad (17)$$

The rather unfamiliar mixture of  $\Delta V$  and  $\Delta F$  in this expression can actually be justified by statistical mechanics. For evaluation we ignore the difference between  $\Delta V$  and  $\Delta F$ . On working out the integral and noting that  $W$  must be greater than  $\frac{1}{2}\Delta V$  (otherwise there is no barrier) we find that

$$\Delta C(T) = \frac{1}{6}\pi^2 k_B^3 T^2 N(0, 0) \{\ln ft + O(1)\}. \quad (18)$$

The time domain of the logarithmic law is given by

$$f^{-1} \ll t \ll f^{-1} \exp(W_0/k_B T), \quad (19)$$

which is not at all restrictive; e.g. if  $f = 10^{10}$  Hz,  $T = 300$  K and  $W_0 = 1$  eV, then the time of measurement can vary between  $10^{-10}$  and  $10^3$  s. The first inequality in

(19) is a condition of validity of equation (16), while the second is derived from the condition  $\tau(W_0, \Delta F) > t$  which prevents the integral over  $W$  from running out to the wings of the distribution.

This time-dependent heat capacity is numerically very small. It is of the order of  $x(k_B T/W_0)^2$  times smaller than the Dulong and Petit value for the matrix, where  $x$  is the atomic fraction of active groups; this fraction could be as large as unity. At low temperatures, the contribution (17) will be overtaken by the tunnelling contribution from the same active groups, which is of order  $xf_i(k_B T/W_0)$  smaller than the Dulong–Petit limit, where  $f_i$  is the fraction of active groups which can tunnel within time  $t$ . Hence tunnelling dominates for temperatures less than  $f_i W_0/k_B \ln ft$ , which is estimated at 30 K if the values  $f_i \sim 0.09$  and  $W_0 \sim 0.6$  eV (with  $f = 10^{10}$  Hz and  $t = 10$  s) given at the end of Section 4 below are used. However, these estimates are somewhat uncertain. For problems of thermal relaxation, Néel's (1949) approximation, while it gives quite accurate algebraic estimates, does less than full justice to the physics. The simple expression (16) for the relaxation time is not strictly correct for thermal experiments where the temperature is time dependent, since the transition rates themselves are temperature dependent. Moreover, temperature relaxation is determined by the internal states of *all* active groups, and so the picture of independently relaxing groups is not correct for thermal problems. A rigorous treatment of this problem is given in the Appendix, where it is shown that thermal relaxation problems involving different kinds of active groups are described by  $s+1$  coupled first-order differential equations. However, the coupling terms, which are due to the temperature dependence of the transition rates, are expected to be small on average, and an explicit perturbation expansion verifies that the first term of this expansion, which is just the Néel result, is adequate in practice.

#### 4. Linear Anelasticity in Glasses

There exists a small body of rather vintage evidence that silicate glasses exhibit well-defined anelastic behaviour within the linear or Hooke's law region. Wiedmann (1886) observed after-effects in many silica-based glasses upon removing a constant load, which were reproducible if the specimens had been allowed to come to equilibrium while loaded. Phillips (1905) first observed a logarithmic-type dependence for a certain silica-based glass fibre, and this was confirmed by other workers. These early observations are described in more detail by Morey (1938). The effects are usually small and are readily observable in only a few materials. While the experiments have been limited to particular materials, we shall assume that these anelastic effects are a universal phenomenon in glasses and differ only in magnitude from one type of glass to another. This assumption follows from the idea that the presence of internal degrees of freedom is a universal feature of the glassy state, which in turn is supported by the apparent universality of the linear specific heat term in glasses at helium temperatures.

Anelasticity thus arises from the coupling of elastic strain to internal degrees of freedom, i.e. to active groups. This coupling is in fact thermodynamic and arises from the strain dependence of the free-energy difference between the two stable states of each active group. If this dependence is known, then the pressure tensor becomes a known function of the populations in the potential wells of all active groups, which individually relax exponentially to new equilibria when the wells are

altered by strain. At this point the advantages of casting the theory in the framework of irreversible thermodynamics become apparent, since these two functional dependences are connected by nothing more complicated than a Maxwell relation for the glass with frozen internal coordinates. There is admittedly an alternative coupling mechanism, namely Onsager cross-coupling between the irreversible flows of mass and of active groups between wells. Here one is limited by the Curie-Prigogine principle (de Groot and Mazur 1962) that forces and fluxes of different tensorial character will not couple. Thus if glass is viewed as a supercooled liquid, coupling could exist between internal transitions and bulk viscous flow (since both are scalar flows), but not to shear flows. Admittedly the experiments reported have not isolated anelasticity in shear deformation, but the Onsager approach in fact raises more questions than it answers and it is simpler to assume that the coupling is purely through normal constitutive or thermodynamic relations.

Formally, one requires the fundamental Gibbs relation for an isotropic material with internal degrees of freedom. This is

$$T dS = dU + V_0 \mathbf{P} : d\mathbf{e} - \sum_{\alpha} \int A^{(\xi)}(q) d\xi^{(\alpha)}(q) dq, \quad (20)$$

where  $\mathbf{P}$  is the pressure tensor,  $\mathbf{e}$  the strain tensor and  $V_0$  the volume of the unstrained material. For the purposes of this paper it is not necessary to prejudge the issue of whether glass exhibits a shear modulus or not; the precise constitutive relation between stress and strain tensors can be left open for the time being. However, the work term in equation (20) can be derived as in standard texts on elasticity (e.g. Love 1892).

Equation (20) leads directly to the Maxwell relation

$$\left( \frac{\delta \mathbf{P}}{\delta \xi^{(\alpha)}} \right)_{T, \mathbf{e}, \xi'} = -V_0^{-1} \left( \frac{\delta A^{(\alpha)}}{\delta \mathbf{e}} \right)_{T, \xi},$$

which connects the dependence of the pressure tensor on degree of advancement to the strain dependence of the affinity. Since  $q$  is a continuous variable these entities are functional derivatives rather than partial derivatives. As quantities held constant in the differentiations,  $\xi$  is  $\{\xi(q)\}$  and  $\xi'$  is  $\{\xi(q); q' \neq q\}$ . A more transparent version follows, from equations (2) and (4), by using the chemical potential  $\tilde{\mu}^{(\alpha)}(q)$  and the internal population  $N^{(\alpha)}(q)$  instead of affinity and degree of advancement:

$$\left( \frac{\delta \mathbf{P}}{\delta N^{(\alpha)}(q)} \right)_{T, \mathbf{e}, N'} = -V_0^{-1} \left( \frac{\delta \tilde{\mu}^{(\alpha)}(q)}{\delta \mathbf{e}} \right)_{T, N} = -V_0^{-1} \mathbf{B}^{(\alpha)}(q). \quad (21)$$

The tensor  $\mathbf{B}(q)$  is the deformation potential  $\delta V(q, \mathbf{e})/\delta \mathbf{e}$  at position  $q$ , and the second equality follows from equation (3) and the fact that  $\mu^{(\alpha)}(q)$  is independent of strain.

The final form of the relation (21) involves the populations  $n_1^{(\alpha)}$  of the lower wells and is thus applicable to high barriers and steady state conditions as discussed in Section 2. To this end we assume that  $N^{(\alpha)}(q)$  is Boltzmann-like in each well, with integrated weights  $n_1^{(\alpha)}$  and  $n_2^{(\alpha)}$  for wells 1 and 2. If the energy barriers from each minimum are greater than  $k_B T$ , then the fraction of active groups which lie in the region near the top of the potential barrier is negligible and we have  $n_1^{(\alpha)} + n_2^{(\alpha)} = N^{(\alpha)}$ . Thus the required derivative is

$$\frac{\partial \mathbf{P}}{\partial n_1^{(\alpha)}} = \int_{-\infty}^{\infty} \frac{\delta \mathbf{P}}{\delta N^{(\alpha)}(q)} \frac{\partial N^{(\alpha)}(q)}{\partial n_1^{(\alpha)}} dq = V_0^{-1} \Delta \mathbf{B}^{(\alpha)}, \quad (22)$$

where  $\Delta \mathbf{B}^{(\alpha)}$  is the difference between the thermal averages of the deformation potentials in the wells. Each thermal average is in fact the strain derivative of the free energy for the well.

The theory of linear elastic response can now be based on the generalization of Hooke's law which includes internal degrees of freedom. This is of the form

$$\mathcal{T}(t) = c e(t) - V_0^{-1} \sum_{\alpha} \Delta B^{(\alpha)} \{n^{(\alpha)}(t) - n_{\text{eq}}^{(\alpha)}\}, \quad (23)$$

where  $\mathcal{T}$  is the stress,  $e$  the strain and  $c$  an elastic modulus for the matrix;  $n^{(\alpha)}$  is  $n_1^{(\alpha)}$ , the population of the lower well of type  $\alpha$ . The tensor character of stress and strain is not essential to the development that follows, so these quantities will be treated as scalars. Note that the second term in equation (23) appears with a negative sign in spite of equation (22) because the stress is tensile and corresponds to a reduction of the pressure tensor. Equation (23) must be supplemented with the rate equations (12) and (13) for active groups, i.e.

$$\dot{n}^{(\alpha)}(t) = -\{n^{(\alpha)}(t) - n_{\text{eq}}^{(\alpha)}(e(t))\} / \tau^{(\alpha)}, \quad (24)$$

where  $\tau^{(\alpha)}$  is given by equation (16) and  $n_{\text{eq}}^{(\alpha)}(e)$  is the equilibrium population of well 1 in the presence of strain, i.e.

$$n_{\text{eq}}^{(\alpha)}(e) = N^{(\alpha)} / [1 + \exp\{-\beta(\Delta F^{(\alpha)} + e \Delta B^{(\alpha)})\}]. \quad (25)$$

Although  $n_{\text{eq}}^{(\alpha)}$  in equation (23) is the value at zero strain, the rate equations predict relaxation to equilibrium in the instantaneous strain field.

It is already obvious that equations (23) and (24) predict memory effects in the stress-strain relationship, as was observed by Wiedmann (1886) and Phillips (1905). The initial-value problem for these equations is such that knowledge of  $\mathcal{T}(0)$  and  $e(0)$  is insufficient to predict  $\mathcal{T}(t)$  for times  $t > 0$ , given a strain function  $e(t)$ . The initial values  $n^{(\alpha)}(0)$  of the populations are required, and these are not completely determined by  $\mathcal{T}(0)$  and  $e(0)$  except in the special case that all active groups are identical. Thus the stress response is a function not only of the initial strain but also of the previous strain history of the sample. It is now understandable that experimental results will not be reproducible unless the sample is first annealed at the measuring temperature. Also, the response to a two-step process, e.g. application of a light stress and then a heavy one, will be dependent on the order in which the stresses are applied and the time duration between their applications. This last result was interpreted by Phillips (1905) as a breakdown of superposition, and one is indeed forced to that conclusion if the applied stresses are regarded as static. In fact, however, the experiment is obviously a dynamic one, and linear superposition is observed if the stresses are regarded as functions of time. From this point of view, the response to the two-step process just mentioned would not be invariant on interchanging the time order of the two steps, since this would give a different stress-time curve. However, Phillips (1905) observed that stress and strain were linearly related in most of his experiments, and linearity implies superposition in the more general sense mentioned.

In what follows, it will be assumed that the glassy sample has been annealed to equilibrium for times  $t > 0$  in a constant strain  $e_0$ . The response to an arbitrary time-varying strain applied at positive times can be expressed in terms of the memory function  $\chi(t)$  or, somewhat more conveniently, Kubo's (1957) relaxation function  $\phi(t)$ , which is the stress response, for  $t > 0$ , to the removal of unit static strain at zero time. It is convenient to consider the general form of the memory function *en route* to  $\phi$ .

Let  $\mathcal{F}_0$  be the equilibrium stress for  $t < 0$  so that, in the linear region,

$$\mathcal{F}_0 = \left( c - V_0^{-1} \sum_{\alpha} \Delta B^{(\alpha)} (\partial n_{\text{eq}}^{(\alpha)} / \partial e)_{e=0} \right) e_0. \quad (26)$$

For  $t > 0$ , the strain is time varying and it is convenient to introduce the quantity  $\delta e(t) = e(t) - e_0$ , the deviation from the previous equilibrium value; this quantity is zero for  $t < 0$ . With similar definitions for other quantities, we then have the rate equations

$$\delta \dot{n}^{(\alpha)}(t) + (\tau^{(\alpha)})^{-1} \delta n^{(\alpha)}(t) = (\tau^{(\alpha)})^{-1} (\partial n_{\text{eq}}^{(\alpha)} / \partial e)_{e=0} \delta e(t). \quad (27)$$

From the Fourier transforms of all such deviations, the AC elastic modulus at frequency  $\omega$  is given by

$$\chi(\omega) \equiv \frac{\delta \mathcal{F}(\omega)}{\delta e(\omega)} = c - V_0^{-1} \sum_{\alpha} \Delta B^{(\alpha)} \frac{(\partial n_{\text{eq}}^{(\alpha)} / \partial e)_{e=0}}{1 + i\omega\tau^{(\alpha)}}. \quad (28)$$

Equivalently we have

$$\delta \mathcal{F}(t) = \int_{-\infty}^t \chi(t-t') \delta e(t') dt', \quad (29)$$

where the memory function  $\chi(t)$  is the Fourier transform of  $\chi(\omega)$ . Since  $\chi(\omega)$  has no poles in the lower half-plane, causality is obeyed and  $\chi(t) = 0$  for  $t < 0$ . Hence the convolution integral can be terminated at  $t' = t$ . An explicit form for the memory function is

$$\chi(t) = c \delta(t) - V_0^{-1} \sum_{\alpha} \frac{\Delta B^{(\alpha)}}{\tau^{(\alpha)}} \left( \frac{\partial n_{\text{eq}}^{(\alpha)}}{\partial e} \right)_{e=0} \exp(-t/\tau^{(\alpha)}) \quad (t > 0). \quad (30)$$

The appearance of the delta function reflects incorrect asymptotic behaviour for  $\chi(\omega)$  at large  $\omega$ ; the correct elastic properties of the matrix have been replaced with the limiting form at low frequencies. This is of no practical importance as anomalous frequency dependences introduced by internal degrees of freedom will occur well below those frequencies (around  $10^{13}$  Hz or greater) where the matrix becomes acoustically dispersive.

The definition of the relaxation function now leads directly to Kubo's (1957) formula

$$\phi(t) = \chi(\omega=0) - \int_0^t \chi(t') dt'. \quad (31)$$

Hence an explicit form for glassy systems is

$$\phi(t) = -V_0^{-1} \sum_{\alpha} \Delta B^{(\alpha)} (\partial n_{\text{eq}}^{(\alpha)} / \partial e)_{e=0} \exp(-t/\tau^{(\alpha)}) \quad (t > 0). \quad (32)$$

Approximate closed expressions in the logarithmic time domain can be obtained by replacing the sum by integrals over the distribution  $N(W, \Delta F, \Delta B)$ . For simplicity,  $\Delta F$  is replaced by  $\Delta V$  and  $\Delta B$  is averaged independently of the other variables. Néel's (1949) approximation is appropriate when the distribution of  $W$  and  $\Delta V$  is flat to order  $k_B T$ ; the exponential is replaced by unity and the integration is restricted to groups with  $\tau(W, \Delta V) > t$ . Hence we obtain

$$\phi(0) = -\frac{1}{2}V_0^{-1}(\Delta B)^2 N(\Delta V=0) \quad (33)$$

and

$$\phi(t) - \phi(0) \approx \frac{1}{2}V_0^{-1}(\Delta B)^2 k_B T N(0,0) \ln ft \quad (34)$$

for times in the logarithmic range (19). Also, we have  $\phi \rightarrow 0$  as  $t \rightarrow \infty$ , as expected on general grounds.

The sizes of these anelastic effects, which are due to the presence of active groups, can be estimated from the parameter  $\alpha$  such that

$$\alpha = (\Delta B)^2 N(\Delta V=0)/2cV_0; \quad (35)$$

$\alpha$  measures the elastic after-effect defined by Wiedmann (1886). In this case we have  $\alpha = |\mathcal{T}(0^+)/\mathcal{T}(0^-)|$ , the ratio of the stresses just after and just before switching off the strain, as may be checked from equations (35), (32) and (26). It applies only when the sample has come to equilibrium for  $t < 0$ . Experimentally, after-effects are generally small (Morey 1938) and are easily observed only in a few cases, apparently glasses containing both potash and soda.

By superposing the responses for steps, one can calculate the response to square pulses, etc. The results of such calculations for a few cases of interest are summarized in Fig. 3. It is noteworthy that the strain response to switching on a stress has a characteristic 'overshoot' past equilibrium; this was observed by Phillips (1905).

Most experimental work has been done with stress as the independent variable, so one now requires analogous formulae for the linear strain response. Again, suppose that the sample has come to equilibrium for  $t < 0$  but under a DC stress  $\mathcal{T}_0$ , and that a time-varying stress  $\delta\mathcal{T}(t)$  is added at positive times. Then the Fourier components of the deviations from past equilibrium determine the AC strain response

$$\mu(\omega) = \delta e(\omega)/\delta\mathcal{T}(\omega) = \chi^{-1}(\omega). \quad (36)$$

Now we have

$$\chi(\omega) = c - \sum_{\alpha} A^{(\alpha)}/(1+i\omega\tau^{(\alpha)}) = c - g(\omega), \quad (37)$$

where the coefficients  $A^{(\alpha)}$  can be identified from equation (28). The corresponding memory function  $\mu(t)$  is given by

$$\mu(t) = \frac{1}{2}\pi^{-1} \int_{-\infty}^{\infty} dt \exp(i\omega t)/\{c - g(\omega)\} \quad (38)$$

and cannot be exhibited in closed form. For practical purposes, it is sufficient to use the geometric series in  $g(\omega)/c$  inside the integral and retain only the first two or so terms, since the series is uniformly convergent if we have  $g(0)/c \equiv \alpha < 1$ . In practice,  $\alpha$  appears to be much smaller than unity in most cases.

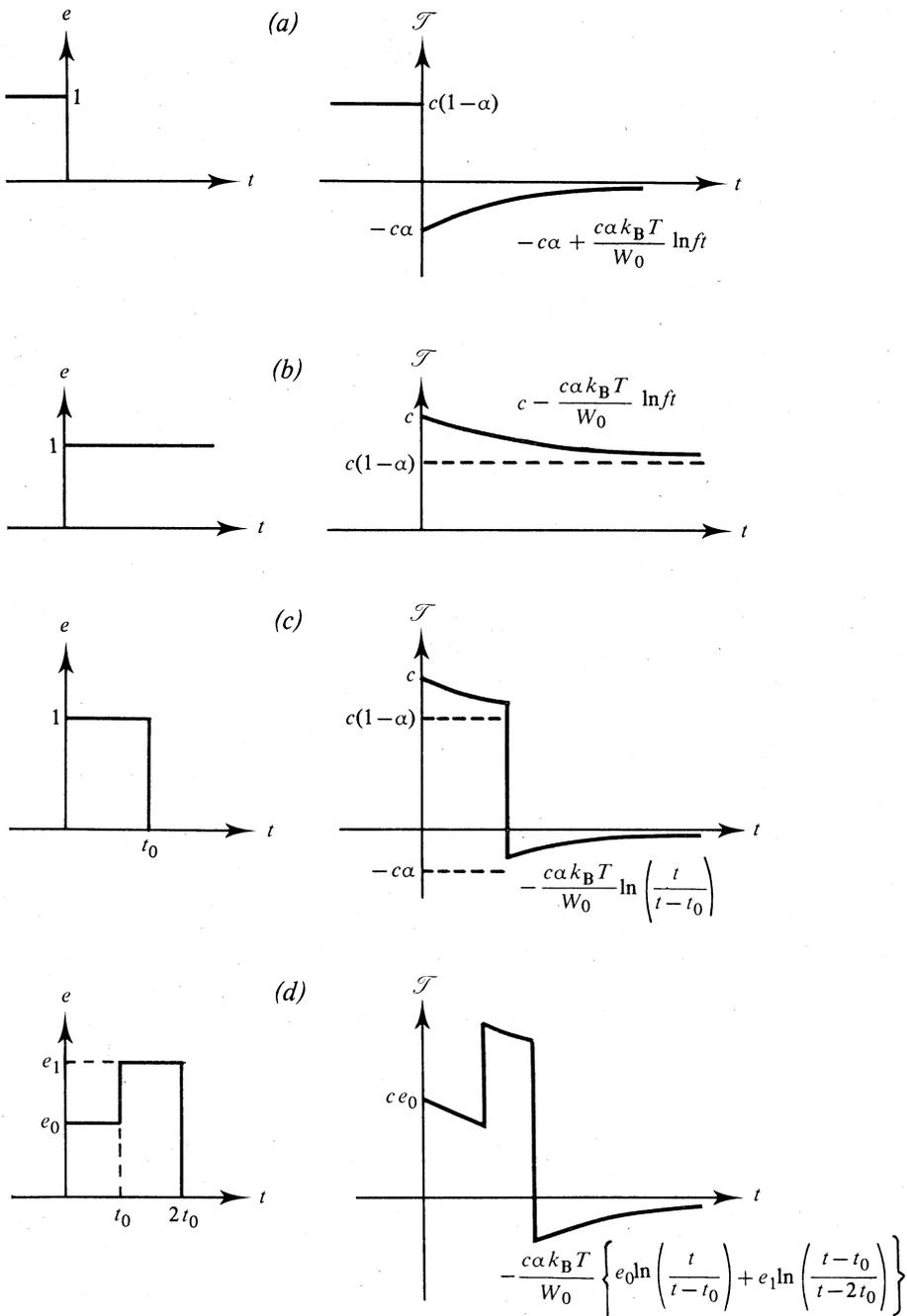
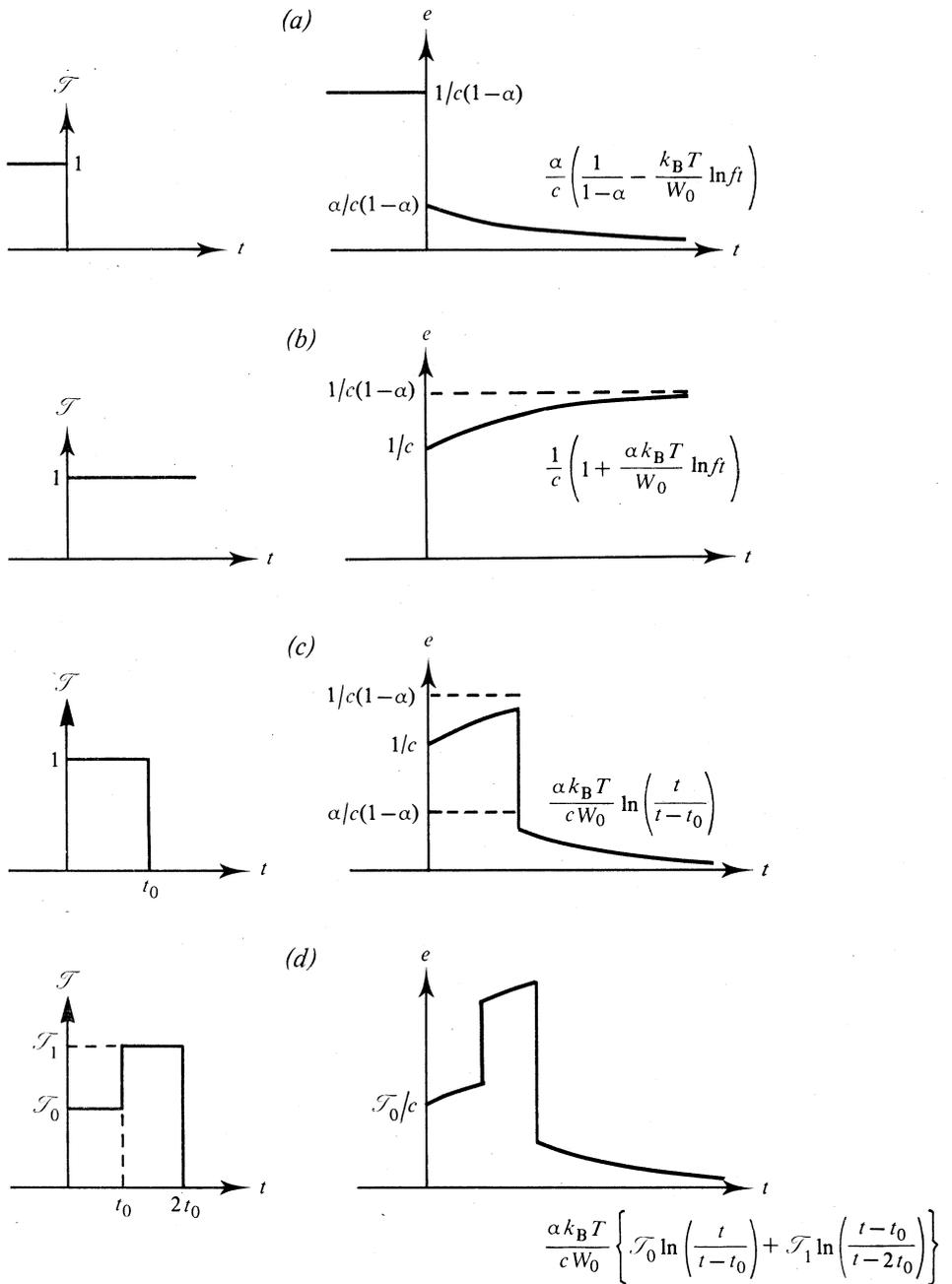


Fig. 3. Schematic representations of stress ( $\mathcal{T}$ ) response to various time-varying applied strains  $e$ : (a) removal of a constant DC strain of unit magnitude at time  $t = 0$ ; (b) application of a unit DC strain at  $t = 0$ ; (c) application of a strain pulse of duration  $t_0$ ; (d) application of a double pulse as shown. Here  $c$  is an elastic modulus for the glass matrix and  $\alpha$  is a measure of the magnitude of elastic after-effects.



**Fig. 4.** Schematic representations of strain ( $e$ ) response to various time-varying applied stresses  $\mathcal{T}$ : (a) removal of a unit DC stress at  $t = 0$ ; (b) application of a unit DC stress at  $t = 0$ ; (c) application of a stress pulse of width  $t_0$ ; (d) application of a double pulse as shown. The expressions quoted are correct only to first order in  $\alpha$ .

The corresponding series for the strain memory function follows by an integration using the analogue of equation (31). Approximate evaluation of group averages in the logarithmic time domain yields

$$\psi(t) = \frac{\alpha}{c(1-\alpha)} - \frac{\alpha k_B T}{cW_0} \ln ft + O(\alpha^2/c), \quad (39)$$

where

$$W_0 = N(\Delta V=0)/N(0,0) \quad (40)$$

is a convenient measure of the width of the distribution in  $W$ .

Some typical applications are as follows. In all cases the analogue of equation (31), and the truncated version (39), are used.

(a) *Switch-off Stress* (Fig. 4a)

A DC stress  $\mathcal{F}$  is removed at  $t = 0$ . The strain response is given by

$$e(t)/\mathcal{F} = \mu(\omega=0) = c^{-1}(1-\alpha)^{-1}, \quad t < 0, \quad (41a)$$

$$= \psi(t), \quad t > 0. \quad (41b)$$

We see that Wiedmann's (1886) elastic after-effect ratio is  $e(0^+)/e(0^-) = \alpha$ .

(b) *Switch-on Stress* (Fig. 4b)

Switch on a DC stress  $\mathcal{F}$  at  $t = 0$ . The response for  $t > 0$  is such that

$$\begin{aligned} e(t)/\mathcal{F} &= \int_0^t \mu(t-t') dt' = \mu(\omega=0) - \psi(t) \\ &= \frac{1}{c} + \frac{\alpha k_B T}{cW_0} \ln ft + \dots, \end{aligned} \quad (42)$$

for  $t$  in the logarithmic range. Just after switch-on, we have  $e(0^+)/\mathcal{F} = c^{-1}$ . Also, the limiting value of  $e(t)/\mathcal{F}$  as  $t \rightarrow \infty$  is  $\mu(\omega=0) = c^{-1}(1-\alpha)^{-1}$ .

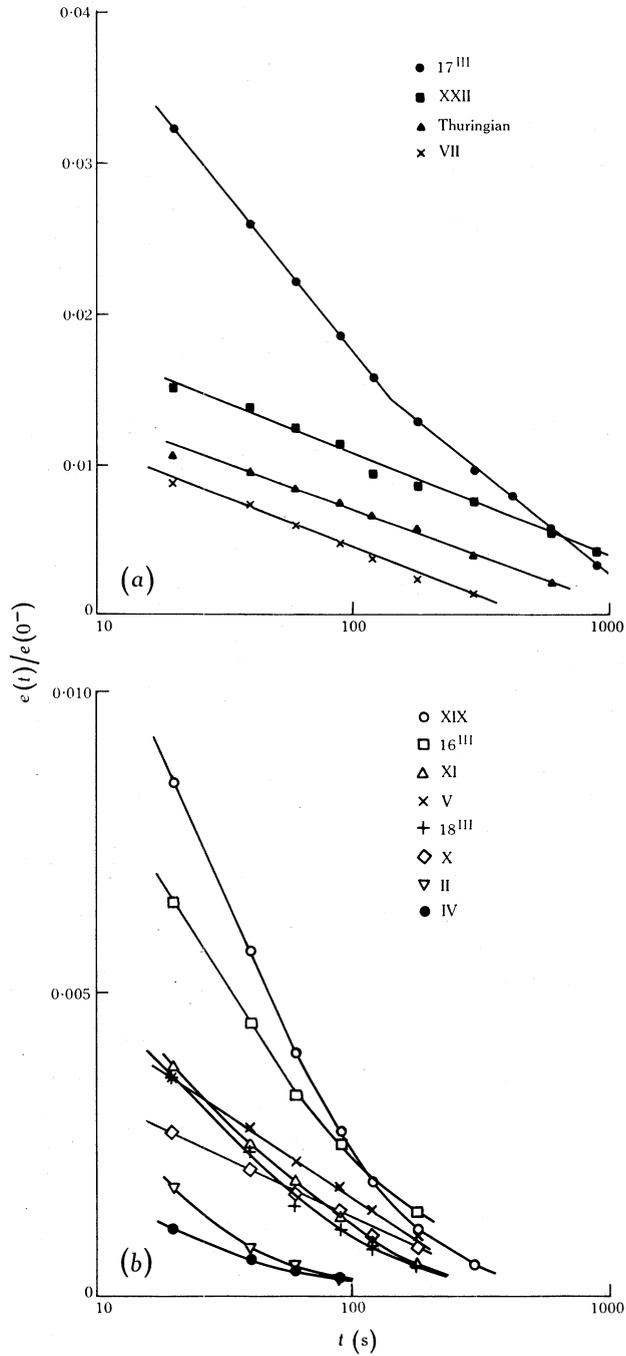
(c) *Square Pulse* (Fig. 4c)

Let  $\mathcal{F}(t) = \mathcal{F}$  for  $0 < t < t_0$ , with the stress zero elsewhere. The strain response is then given by the result of (b) above for times between 0 and  $t_0$ . For  $t > t_0$ , the response is

$$\begin{aligned} e(t)/\mathcal{F} &= \int_0^{t_0} \mu(t-t') dt' = \psi(t-t_0) - \psi(t) \\ &\approx \frac{\alpha k_B T}{cW_0} \ln \left( \frac{t}{t-t_0} \right), \end{aligned} \quad (43)$$

for  $t$  and  $t_0$  in the logarithmic range (19). This formula does not hold for  $f(t-t_0) \lesssim 1$ . At  $t = t_0^+$  we have

$$e(t_0^+)/\mathcal{F} = (\alpha k_B T/cW_0) \ln ft_0. \quad (44)$$



**Fig. 5.** Graphical presentation of Wiedmann's (1886) elastic after-effect measurements for silica glasses, plotted logarithmically against time  $t$ . The load was removed at  $t = 0$ . All 12 specimens had different chemical compositions, as given in the original paper.

As shown in Fig. 4c, the jump discontinuities at both  $t = 0$  and  $t_0$  reflect the purely elastic response of the matrix, i.e.  $\Delta e/\mathcal{T} = \pm c^{-1}$ .

(d) *Two-step Pulse* (Fig. 4d)

Let a constant strain  $\mathcal{T}_0$  be applied over the time interval  $0-t_0$ , and a strain  $\mathcal{T}_1$  over the interval  $t_0-2t_0$ . Only the strain response for times in excess of  $2t_0$  will be considered; it is given by

$$\begin{aligned} e(t) &= \int_{-\infty}^t \mu(t-t') \mathcal{T}(t') dt' = \mathcal{T}_0 \{\psi(t-t_0) - \psi(t)\} + \mathcal{T}_1 \{\psi(t-2t_0) - \psi(t-t_0)\} \\ &= \frac{\alpha k_B T}{c W_0} \left\{ \mathcal{T}_0 \ln \left( \frac{t}{t-t_0} \right) + \mathcal{T}_1 \ln \left( \frac{t-t_0}{t-2t_0} \right) \right\}. \end{aligned} \quad (45)$$

Both logarithms are positive as  $t > 2t_0$ . Moreover, the second logarithm is greater than the first. Suppose now that  $\mathcal{T}_0 < \mathcal{T}_1$ , that is, a light stress is followed by a heavy stress. It then follows that the response after all stress is removed is larger than it would be if the magnitudes  $\mathcal{T}_0$  and  $\mathcal{T}_1$  were interchanged, i.e. a heavy stress followed by a light stress. This is just what is expected from a material with fading memory, and is what Wiedmann (1886) observed.

The logarithmic time law was first reported in the literature by Phillips (1905). However, Wiedmann's (1886) results also show logarithmic behaviour in some cases, and as his experiments are more comprehensive than those of Phillips they will be analysed here in detail.

Wiedmann (1886) observed elastic after-effects in 12 different types of silica glass (specified in the original paper) upon removal of applied stress. His results are given in terms of the elastic after-effect ratio  $e(t)/e(0^-)$  and, as Wiedmann claims that this quantity was independent of the initial load, it can be assumed that the linear or Hooke's law regime is appropriate. Fig. 5 shows his tabulated results plotted against  $\ln t$ . It will be observed that in eight cases there is a linear region, extending over the entire period of observation in some cases but otherwise transforming to a more slowly varying function at large times. The linear regions can be fitted to the form

$$e(t)/e(0^-) = \alpha \{1 - (k_B T/W_0) \ln ft\} \quad (f^{-1} \ll t \ll f^{-1} \exp(\beta W_0)), \quad (46)$$

which follows from equations (41b), (41a) and (39), for  $\alpha \ll 1$ . The fitting procedure cannot determine the three unknown parameters  $\alpha$ ,  $W_0$  and  $f$  uniquely but the first two will be fairly insensitive to variations in  $f$  as it appears as  $\ln f$  in equation (46). A rough estimate for this quantity, which is the rate of phonon-assisted attempts at transitions over the potential barrier, may be made using the kind of analysis given by Jäckle (1972) and Black (1978); the result is  $f \sim 10^{11}$  Hz at 300 K. This estimate is rather uncertain. Table 1 shows the values of  $\alpha$  and  $W_0$  obtained for  $f$  between  $10^8$  and  $10^{12}$  Hz, which spans all reasonable values. The consequent variations in  $\alpha$  and  $W_0$  are relatively minor. It can be seen that  $\alpha$  is typically of order 0.01–0.1 but is larger in one exceptional case. Moreover, the width  $W_0$  of the distribution of energy barriers lies between 0.6 and 0.9 eV, which is larger than the value of 0.1 eV obtained by equating  $W_0$  with the melting energy. To obtain values of this order from Wiedmann's data requires unacceptably small values of  $f$ .

**Table 1. Quantities derived from Wiedmann's (1886) elastic after-effect measurements**

The specimens listed are those that could be fitted by an  $\ln t$  law. The various parameters are defined in the text. For fitting these parameters, the temperature was taken to be 300 K

Sample	$Q$	$t_m$ (s)	$f = 10^8$ Hz			$f = 10^{10}$ Hz			$f = 10^{12}$ Hz		
			$W_0$ (eV)	$\alpha$	$\Delta B$ (eV)	$W_0$ (eV)	$\alpha$	$\Delta B$ (eV)	$W_0$ (eV)	$\alpha$	$\Delta B$ (eV)
17 <sup>III</sup>	6.5	670	0.64	0.23	3.0	0.76	0.27	3.2	0.88	0.31	3.5
XXII	8.1	3300	0.69	0.079	1.8	0.80	0.093	1.9	0.92	0.11	2.1
Thuringian	7.2	1300	0.66	0.070	1.7	0.78	0.082	1.8	0.90	0.095	1.9
VII	6.1	450	0.63	0.073	1.7	0.75	0.087	1.8	0.87	0.10	1.9
XIX	5.1	160	0.61	0.096	1.9	0.73	0.115	2.1	0.85	0.13	2.3
16 <sup>III</sup>	5.1	160	0.61	0.070	1.7	0.73	0.084	1.8	0.85	0.10	1.9
V	5.7	300	0.62	0.029	1.1	0.74	0.035	1.2	0.86	0.040	1.3
X	6.1	450	0.63	0.021	0.9	0.75	0.025	1.0	0.87	0.029	1.1

The two quantities that follow directly from fitting to equation (46) are the slope  $\alpha k_B T/W_0$  and an intercept, or equivalently the parameter

$$Q = W_0/k_B T - \ln f. \quad (47)$$

$Q$  has some significance, as  $t_m = f^{-1} \exp(W_0/k_B T) = \exp Q$  is the upper limit of the time range of the logarithmic law. The values of  $t_m$  listed in Table 1 correlate very well with the ends of the logarithmic regions in Wiedmann's (1886) data (Fig. 5), which is strong evidence that the theory is applicable here.

Finally, we note that rough estimates for the deformation potential  $\Delta B$  follow from those for  $\alpha$  by using equation (35). For this purpose, universal values of the elastic modulus  $c$  and the density of states  $N(\Delta V=0)$  were used, namely  $c \sim 5 \times 10^{11} \text{ dyn cm}^{-2}$  ( $\equiv 5 \times 10^{10} \text{ Pa}$ ) and  $N(\Delta V=0)/V_0 \sim 1 \times 10^{-34} \text{ erg}^{-1} \text{ cm}^{-3}$  ( $\equiv 10^{-21} \text{ J}^{-1} \text{ m}^{-3}$ ). The latter value is representative of results from low temperature tunnelling properties of various fused silicas (Black 1978). There is order of magnitude agreement with the value of 3.2 eV quoted by Black and Halperin (1977), derived from the phonon-echo experiments of Golding and Graebner (1976) and the ultrasonic attenuation work by Golding *et al.* (1976).

## 5. Thermal Creep

The delayed thermal contraction of glasses after cooling from the melt (Morey 1938) is one of the oldest and best known of the anelastic effects. It is due to delayed thermalization of active groups after a temperature change, rather than a strain-induced change in the internal potentials. The basic stress-strain law (23) and the internal rate equations (24) enable the effect to be treated quantitatively. It will be sufficient to give the linear version of the theory, where the temperature change is small.

Let a glass sample be in equilibrium at temperature  $T_0$  for times  $t < 0$ , and let the temperature be abruptly increased by  $\delta T$  at  $t = 0$ . It is assumed that the sample is not mechanically constrained in any way during this process, so that the normal instantaneous thermal expansion will take place. This expansion should not be counted as strain, since strain is always referred to the equilibrium state at the current temperature. Final equilibrium is not reached until the active groups have thermalized at temperature  $T_0 + \delta T$ , and the approach to this equilibrium is accompanied by the disappearance of the strain that was generated by raising the temperature.

From equation (24), the population of active groups of type  $\alpha$  in the lower wells will be such that

$$n^{(\alpha)}(t) = n_{\text{eq}}^{(\alpha)}(T_0) + (dn_{\text{eq}}^{(\alpha)}/dT_0) \delta T \{1 - \exp(-t/\tau^{(\alpha)})\}. \quad (48)$$

The expansion occurs at zero stress, so that equation (23) gives a thermally induced strain

$$\begin{aligned} e(t) &= (cV_0)^{-1} \sum_{\alpha} \Delta B^{(\alpha)} \{n^{(\alpha)}(t) - n_{\text{eq}}^{(\alpha)}(T_0 + \delta T)\} \quad (t > 0) \\ &\approx \frac{\delta T}{4cV_0 k_B T_0^2} \int_0^{\infty} dW \int_0^{\infty} d\Delta V \int_{-\infty}^{\infty} d\Delta B N(W, \Delta V, \Delta B) \Delta B \Delta V \operatorname{sech}^2\left(\frac{\Delta V}{2k_B T}\right) \\ &\quad \times \exp\left(-\frac{t}{\tau(W, \Delta V)}\right). \end{aligned} \quad (49)$$

Note that  $\Delta B$  ranges over positive and negative values even though  $\Delta V$  is, by definition, positive. It is now clear that there will be no thermal creep unless  $\Delta B$  and  $\Delta V$  are correlated. For this purpose of evaluation, let us assume that they are completely correlated in sign but uncorrelated in magnitude. Then the methods used earlier lead to

$$\frac{e(0)}{\delta T} = \frac{k_B \langle \Delta B \rangle}{cV_0} N(\Delta V = 0), \quad \frac{e(t) - e(0)}{\delta T} = -\frac{k_B^2 T_0 \langle \Delta B \rangle}{cV_0} N(0, 0) \ln ft, \quad (50)$$

for  $t$  in the logarithmic range (19); here the angle brackets denote an average over active groups. A more realistic assumption might be that the ratio  $\Delta B/\Delta V$  is of one sign and uncorrelated with  $\Delta V$  and  $W$ , but the essential features of the result are not changed. For the signs of equations (50) to agree with observation it is necessary that  $\langle \Delta B \rangle$  be negative, as creep normally proceeds in the same direction as the instantaneous length change from the thermal expansion of the matrix (see Fig. 6). This is a surprising result, since there seems to be no compelling reason why  $\langle \Delta B \rangle$  should be negative for all glasses.

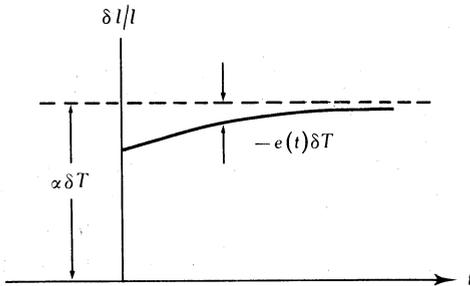


Fig. 6. Relationship of a time-dependent strain  $e(t)$  to the total linear expansion  $\delta l/l$  resulting from a sudden temperature rise  $\delta T$ . In this figure,  $\alpha$  is the linear expansion coefficient of the matrix.

## 6. Dispersion and Damping of Sound Waves

As is well known, anelasticity will cause dispersion and damping in the propagation of ultrasonic waves. This topic has a long history; the methods of irreversible thermodynamics were used by Meixner (1943, 1952) and others to treat the same problem for internal relaxation in molecular gases, and a particular example was

treated by Einstein (1920). More recently, relaxation damping in glasses was considered by Jäckle *et al.* (1976), whose analysis parallels ours in some respects. The theory is as follows.

All sources of damping other than internal degrees of freedom are excluded from consideration, it being assumed that they can be restored additively at the end of the calculation. It is convenient to assume that the sound waves are adiabatic, which is the case for sufficiently low frequencies. Specifically, one requires

$$\omega \ll v^2 \rho c_V / \kappa, \quad (51)$$

where  $v$  is the sound velocity,  $\rho$  the mass density,  $c_V$  the specific heat per unit mass and  $\kappa$  the thermal conductivity. For vitreous silica at room temperature, the right-hand side is  $\sim 10^{11}$  Hz, so the inequality (51) is usually obeyed. The appropriate constitutive equation between stress and strain is therefore the adiabatic one:

$$\mathbf{P}(\mathbf{r}, t) = P_0 \mathbf{1} - K_S (\text{tr } \mathbf{e}) \mathbf{1} - 2G_S (\mathbf{e} - \frac{1}{3} \text{tr } \mathbf{e} \mathbf{1}) + \sum_{\alpha} \Delta \mathbf{B}^{(\alpha)} (n^{(\alpha)}(\mathbf{r}, t) - n_{\text{eq}}^{(\alpha)}), \quad (52)$$

where  $K_S$  and  $G_S$  are adiabatic bulk and shear moduli, and  $P_0$  is the equilibrium hydrostatic pressure. Note that the factor  $V_0^{-1}$  is omitted from the last term; the populations  $n^{(\alpha)}$  are now interpreted as volume densities at the point where the pressure tensor is measured.

The wave equation follows by substitution in the balance equation for momentum density, as described by Jäckle *et al.* (1976), for example. In this way the dispersion relation is obtained as the vector equation

$$\left(\frac{\omega}{k}\right)^2 \rho_0 \hat{\mathbf{u}} = (K_S + \frac{1}{3} G_S) \hat{\mathbf{k}} \cdot \hat{\mathbf{u}} \hat{\mathbf{k}} + G_S \hat{\mathbf{u}} - \frac{1}{4k_B T V_0} \sum_{\alpha} \frac{N^{(\alpha)} \text{sech}^2(\frac{1}{2} \beta \Delta F^{(\alpha)})}{1 + i\omega\tau^{(\alpha)}} \hat{\mathbf{k}} \cdot \Delta \mathbf{B}^{(\alpha)} \Delta \mathbf{B}^{(\alpha)} \hat{\mathbf{k}} \hat{\mathbf{u}}, \quad (53)$$

where circumflexes denote unit vectors, and  $\hat{\mathbf{u}}$  is a polarization vector. At high frequencies the contribution of active groups vanishes and the usual separation into longitudinal and transverse modes occurs with  $\omega$  linear in  $k$ . The coefficients are the expected sound velocities for an isotropic solid. At finite frequencies, the same separation occurs if the principal axes of the deformation potential tensors  $\Delta \mathbf{B}^{(\alpha)}$  are randomly distributed. If the average over principal axes can be effected independently of the group sum, then that first average yields an isotropic fourth-rank tensor, i.e.

$$\langle \Delta \mathbf{B}_{ij}^{(\alpha)} \Delta \mathbf{B}_{kl}^{(\alpha)} \rangle = (b_l^2 - 2b_t^2) \delta_{ij} \delta_{kl} + b_t^2 (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}). \quad (54)$$

This is the general form (Jeffreys 1931) for an isotropic fourth-rank tensor which is an average of products of two symmetric second-rank tensors. It is sufficient to show that equation (53) now yields separate longitudinal and transverse modes at all frequencies. For either case there is a scalar dispersion relation of the form

$$\left(\frac{\omega}{k}\right)^2 \rho = c - \frac{b^2}{4k_B T V_0} \sum_{\alpha} \frac{N^{(\alpha)} \text{sech}^2(\frac{1}{2} \beta \Delta F^{(\alpha)})}{1 + i\omega\tau^{(\alpha)}}, \quad (55)$$

where  $b$  is  $b_l$  for longitudinal waves and  $b_t$  for transverse waves, and  $c$  is the appropriate elastic modulus.

An approximate evaluation of the group sum in equation (55) can be done when the distributions are flat over thermal energies. An obvious analogue of the Néel (1949) technique can be used to estimate the real part; in fact this is the first term in a systematic expansion which has been given in a different context by Rozario and Smith (1977). The next term gives an estimate of the imaginary part. Hence

$$(\omega/k)^2 = v(\omega)^2 + i w(\omega)^2, \quad (56)$$

where

$$v(\omega)^2 = (c/\rho)(1-\alpha), \quad \omega = 0, \quad (57a)$$

$$= (c/\rho)\{1 - (\alpha k_B T/W_0) \ln(f/\omega)\}, \quad f \exp(-\beta W_0) \ll \omega \ll f, \quad (57b)$$

$$= c/\rho, \quad \omega \rightarrow \infty, \quad (57c)$$

and also  $\alpha = b^2 N(\Delta V=0)/2cV_0$ , in analogy with equation (35). Here  $v(\omega)$  is the approximate sound velocity obtained by neglecting damping. The imaginary part  $w^2$  is constant at the value  $\pi c \alpha k_B T/2\rho W_0$  in the logarithmic frequency range between  $f \exp(-\beta W_0)$  and  $f$ , goes linearly to zero for  $\omega \rightarrow 0$  and goes to zero as  $\omega^{-1}$  for  $\omega \rightarrow \infty$ . It is now obvious that the damping is small, at least in the sense that  $v(\omega)$  is a good approximation to the actual sound velocity, because the ratio of imaginary and real parts is of order  $k_B T/W_0$  which is typically  $10^{-2}$ – $10^{-3}$ . Thus the sound velocity is weakly dispersive, varying logarithmically with frequency, over a wide frequency range which might typically extend from  $10^{10}$  to  $10^{-3}$  Hz.

Damping may be measured by the extinction coefficient, or inverse mean free path which is twice the imaginary part of  $k$  for real  $\omega$ . Now we have

$$-2 \operatorname{Im} k \approx \omega w(\omega)^2/v(\omega)^3,$$

from which it appears that the damping varies linearly with  $\omega$  in the logarithmic range, goes quadratically to zero as  $\omega \rightarrow 0$  and tends to a constant value as  $\omega \rightarrow \infty$ . This last result is physically incorrect and should not be used since the Fokker-Planck equation (7), which leads to the relaxation time approximation, breaks down for frequencies greater than  $f$ . Using the value quoted for  $w^2$  in the logarithmic frequency range and values given elsewhere for other parameters, we estimate the extinction coefficient for a typical silica glass as  $10^{-8} \omega \text{ cm}^{-1}$ . This value is comparable with the relaxational tunnelling contribution estimated by Jäckle (1972) at high temperatures and low frequencies, and has the same (linear) frequency dependence.

There is no sign of such absorption in glasses in the high temperature region, say above 100 K, where the theory should apply. What is observed (Hunklinger and Arnold 1976, and references therein) is the classical attenuation due to thermal conduction which varies as the square of the frequency, for which the inverse mean free path is

$$l^{-1} = (\omega^2 T/\rho v_s^2)(\alpha \kappa_T/\rho c_V)^2.$$

Here  $\alpha$  is the volume expansion coefficient and  $\kappa_T$  the thermal conductivity. The corresponding numerical estimate is  $10^{-22} \omega^2 \text{ cm}^{-1}$ , which is close to observed values (Lamb *et al.* 1959). On this basis, the contribution of active groups would dominate for frequencies less than  $10^{14}$  Hz, in clear contradiction to observation.

Several ways out of this difficulty come to mind. It is always possible that the distributions of  $W$  and  $\Delta V$  are not flat to about 1 eV but much narrower, in which case the anomalous linear frequency dependence of the damping would not occur and the damping would be concentrated in a narrow frequency band. The success of the original model in describing elastic after-effects works against this. The possibility that the active group contribution is not observed through saturation of the populations of the upper potential wells can be ruled out, since this would require strain fields of the order of  $k_B T/\Delta B$ , which implies enormously large sound power densities, of the order of  $10^4 \text{ W cm}^{-2}$ . The most promising explanation is that the concentration of active groups is large enough for indirect coupling between them, as described by Joffrin and Levelut (1975), to open up strong relaxation paths, thereby bringing active groups much closer to equilibrium. Unfortunately, the model developed here cannot cope with such effects in its present form, since the Maxwell relation (22) cannot describe the local stress field around each active group. This must be reserved as a future problem. Meanwhile, it should not be concluded that the absence of absorption from active groups is an adverse reflection on the AHV-Phillips model, either in its quantum or classical forms.

## 7. Concluding Discussion

The AHV-Phillips model for the low temperature properties of glasses, in which a number of localized active groups exhibit internal degrees of freedom with two stable states, has been generalized here to higher temperatures where internal equilibrium is achieved by thermal activation rather than quantum mechanical tunnelling. The model has been applied to a number of time-dependent phenomena and compared with experiment where possible. In this section the model is set in context by comparing it and its predictions with other theories of the glassy state.

The idea of internal degrees of freedom in glasses is certainly not new; quasi-thermodynamic treatments based on one, or at most two, internal thermodynamic variables may be found in the literature, and such treatments have been linked with the irreversible thermodynamic approach in the review article by Davies and Jones (1954). This approach understandably generates predictions which are not in accord with experiment, through lack of a sufficient number of internal variables. The present approach, which requires a continuous distribution of active groups of different kinds, is capable of resolving all such discrepancies. However, the model can claim to be slightly more than a heuristic invention, as the description of active groups is necessarily microscopic, at least if one assumes that these groups are made up of small numbers of tightly bound atoms. The existence of such entities is indirectly confirmed by a variety of low temperature experiments, referred to elsewhere throughout this paper. They have also been observed in a computer simulation for a tetrahedrally-coordinated random network glass (Smith 1979).

The detailed analysis of Wiedmann's (1886) elastic after-effect measurements has led to estimates of 0.6–0.9 eV for  $W_0$ , the width of the distribution of the average energy barrier between wells. This quantity is not accessible from the low temperature experiments, and the question arises whether these values are compatible with existing information from tunnelling experiments. We have already noted that the deformation potentials  $\Delta B$  obtained from these two areas are similar. Now the width of the distribution of  $\Delta V$ , the difference between potential minima, is likely to be of the

same order as  $W_0$ ; certainly it cannot be much greater since we have  $W > \frac{1}{2} \Delta V$  for each active group. The quantity extracted from the tunnelling specific heat in glasses (Black 1978) is  $N(\Delta V=0) f_t$ , where  $f_t$  is the fraction of atoms that tunnel. The value of  $f_t$  cannot be measured directly, but may be estimated at 0.1 or thereabouts (Smith 1979), leading to  $N(\Delta V=0) \approx 0.7 \text{ eV}^{-1} \text{ atom}^{-1}$  for fused silica. If the width of this distribution is 0.7 eV, then the total number of active groups (the area under the curve) must be of order 1 per atom. This figure is possibly too high, but the precise value is not of practical importance as only a small fraction of these groups can be excited, either by phonon-assisted tunnelling or by thermal activation.

All the phenomena described in this paper which arise from thermally activated transitions can, and will, occur by tunnelling through the same potential barrier. There is little experimental information that enables one to distinguish the thermally activated and the tunnelling regimes. Suitable experiments might provide some information on the identity of active groups in these two regimes; it is certainly not obvious that active groups which are thermally activated at high temperatures can be put into one to one correspondence with those that tunnel at low temperatures. Even if such a correspondence could be made, the potential in which each group moves will be temperature dependent as it arises cooperatively from frozen disorder in the glass. As the temperature is raised to the glass temperature, i.e. the rather loosely defined temperature at which the liquid freezes to a glass, the number of active groups must shrink to zero, since there can be no atoms or groups of atoms which see double-well potentials in the liquid state. In this paper such potentials were assumed to be fixed; this is probably a reasonable approximation only if the temperature is a small fraction of the glass temperature.

Because each double-well potential arises from the disposition of neighbouring atoms in the glass, it should not be regarded as truly static even at the lowest temperatures. There is always the possibility that surrounding motions can slowly transform such a potential into one with a single minimum, and there is some evidence for this from computer simulations, both for random-network glasses and for the so-called spin glasses (Kirkpatrick 1977). Local atomic motion also leads to coupling between active groups (Joffrin and Levelut 1975; Black and Halperin 1977).

The atomic picture of glass structure and dynamics presented by the AHV-Phillips model is in stark contrast with the much older view that glasses are merely very viscous supercooled liquids, an idea which goes back to Lewis and Gibson (1920) and which gained support from Simon and Lange's (1926) demonstration that glassy glycerol violates the Nernst heat theorem. It is not the purpose of this paper to consider this issue in detail, but it is obvious that a supercooled liquid has very different anelastic properties from the AHV-Phillips model glass. The former implies no lasting shear rigidity, with a Newtonian resistance to shear deformation proportional to the rate of change of strain. Hence a supercooled liquid to which a sudden shear stress is applied will deform linearly in time. The recognition that some permanent resistance to shear stress is required to saturate the strain-time curve is presumably responsible for the heuristic viscoelastic theories, which posit shear viscosity and a shear modulus in the same substance. However, this hypothetical substance would then exhibit an exponential approach to saturation in the strain-time curve, and the original viscoelastic model must be transformed into a pseudo-microscopic version with a continuous distribution of relaxation times to produce the logarithmic time dependence observed in polymers (Ferry and Williams 1952;

Ferry 1961) and glasses. This final viscoelastic model now bears almost no relation to a supercooled liquid. However, a version of it exists which corresponds exactly to the classical behaviour of the AHV–Phillips model.

The mechanical ‘circuit element’ models of viscoelasticity fall into two basic classes, namely Maxwell models in which springs (elastic elements) and dashpots (viscous elements) are connected in series, and Voigt models, in which they are in

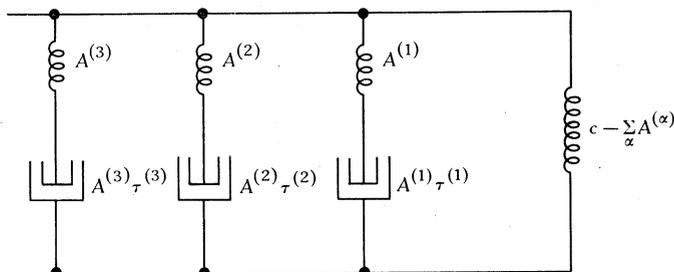


Fig. 7. Equivalent mechanical circuit of the AHV–Phillips model, as expressed by the AC elastic modulus of equation (37).

parallel (Mason 1958). The Maxwell (1867, 1868) model is thought to be appropriate for liquids, since the AC elastic modulus (stress–strain) of the series combination is dominated by the viscous element at low frequencies. Similarly, the Voigt (1892) model is intended for solids; the parallel combination looks like a pure spring at low frequencies. These expectations are not quite borne out by the form of the AC response function (37) of Section 4, namely

$$\mathcal{F}(\omega)/e(\omega) = c - \sum_{\alpha} A^{(\alpha)} / (1 + i\omega\tau^{(\alpha)}).$$

The most obvious equivalent circuit is a parallel combination of Maxwell elements, with spring constants  $A^{(\alpha)}$  and dashpot constants  $A^{(\alpha)}\tau^{(\alpha)}$  (Fig. 7). A parallel spring of stiffness  $c - \sum_{\alpha} A^{(\alpha)}$  is needed to produce elastic resistance at zero frequency; note that this last spring cannot be identified solely with the matrix, which has stiffness  $c$ . In fact, the irrelevance of these equivalent circuits is highlighted by the fact that equation (37) can also be represented by a series combination of Voigt elements, although with more complicated expressions for the element constants.

To summarize, it is assumed that the matrix in which active groups are embedded is basically a solid; it is neither necessary nor desirable for this matrix to exhibit shear viscosity in the macroscopic sense. If this is correct, then a glass will be distinguished from a liquid, supercooled or otherwise, by having a true shear modulus, and if any given substance can exist in both phases there must then be a phase transition between them. Circumstantial evidence for a phase transition exists in the Vogel–Tamman–Fulcher law for transport properties of glass-forming liquids, by which different transport coefficients diverge at a common temperature  $T_0$  (Angell and Moynihan 1969; Rao and Rao 1978). A more direct experimental test would be to look for the onset of true shear resistance as the temperature is lowered. This is unlikely to be straightforward, as measurements over very different time scales will be necessary to ensure that shear resistance observed over a finite time does not extrapolate to zero as the time scale is extended indefinitely.

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## References

- Anderson, P. W., Halperin, B. I., and Varma, C. M. (1972). *Philos. Mag.* **25**, 1.
- Angell, C. A., and Moynihan, C. T. (1969). In 'Molten Salts' (Ed. G. Mamantov) (Marcel Dekker: New York).
- Black, J. L. (1978). *Phys. Rev. B* **17**, 2740.
- Black, J. L., and Halperin, B. I. (1977). *Phys. Rev. B* **16**, 2879.
- Brown, W. F., Jr (1963). *Phys. Rev.* **130**, 1977.
- Davies, R. O., and Jones, G. O. (1954). *Adv. Phys.* **2**, 370.
- Einstein, A. (1920). *Sitzungsber. K. Preuss. Akad. Wiss.* No. 380.
- Ferry, J. D. (1961). 'Viscoelastic Properties of Polymers' (Wiley: New York).
- Ferry, J. D., and Williams, M. L. (1952). *J. Colloid Sci.* **7**, 347.
- Golding, B., and Graebner, J. E. (1976). *Phys. Rev. Lett.* **37**, 852.
- Golding, B., Graebner, J. E., and Schutz, R. J. (1976). *Phys. Rev. B* **14**, 1660.
- Goubau, W. M., and Tait, R. A. (1975). *Phys. Rev. Lett.* **34**, 1220.
- de Groot, S. R., and Mazur, P. (1962). 'Non-equilibrium Thermodynamics' (North-Holland: Amsterdam).
- Halperin, B. I. (1976). *Ann. N.Y. Acad. Sci.* **279**, 173.
- Hunklinger, S., and Arnold, W. (1976). In 'Physical Acoustics', Vol. 12 (Eds W. P. Mason and R. N. Thurston) (Academic: New York).
- Jäckle, J. (1972). *Z. Phys.* **257**, 212.
- Jäckle, J., Piché, L., Arnold, W., and Hunklinger, S. (1976). *J. Non-cryst. Solids* **20**, 365.
- Jeffreys, H. (1931). 'Cartesian Tensors' (Cambridge Univ. Press).
- Joffrin, J., and Levelut, A. (1975). *J. Phys. (Paris)* **36**, 811.
- Kirkpatrick, S. (1977). *Phys. Rev. B* **16**, 4630.
- Kubo, R. (1957). *J. Phys. Soc. Jpn* **12**, 570.
- Kummer, R. B., Dynes, R. C., and Narayanamurti, V. (1978). *Phys. Rev. Lett.* **40**, 1187.
- Lamb, J., Redwood, M., and Shteinshleifer, Z. (1959). *Phys. Rev. Lett.* **3**, 28.
- Lewis, G. N., and Gibson, G. E. (1920). *J. Am. Chem. Soc.* **42**, 1529.
- Love, A. E. H. (1892). 'A Treatise on the Mathematical Theory of Elasticity' (Cambridge Univ. Press); 4th edn (1944) (Dover: New York).
- Mason, W. P. (1958). 'Physical Acoustics and the Properties of Solids' (Van Nostrand: Princeton, N.J.).
- Maxwell, J. C. (1867). *Philos. Trans. R. Soc. London* **157**, 49.
- Maxwell, J. C. (1868). *Philos. Mag.* (4) **35**, 129, 185.
- Meixner, J. (1943). *Ann. Phys. (Leipzig)* (5) **43**, 470.
- Meixner, J. (1952). *Acoustica* **2**, 101.
- Meixner, J. (1957). *Z. Phys.* **149**, 624.
- Morey, G. W. (1938). 'The Properties of Glass' (Am. Chem. Soc.: Washington, D.C.).
- Néel, L. (1949). *Ann. Geophys.* **5**, 99.
- Phillips, P. (1905). *Philos. Mag.* **9**, 512.
- Phillips, W. A. (1972). *J. Low Temp. Phys.* **7**, 351.
- Prigogine, I., and Mazur, P. (1953). *Physica* **19**, 241.
- Rao, C. N. R., and Rao, K. J. (1978). 'Phase Transitions in Solids' (McGraw-Hill: New York).
- Rozario, F. A., and Smith, D. A. (1977). *J. Phys. F* **7**, 439.
- Simon, F. E., and Lange, F. (1926). *Z. Phys.* **38**, 227.
- Smith, D. A. (1979). *Phys. Rev. Lett.* **42**, 729.
- Voigt, W. (1892). *Ann. Phys. (Leipzig)* **47**, 671.
- Wiedmann, G. (1886). *Ann. Phys. Chem. (Leipzig)* **29**, 214.
- Woods, L. C. (1975). 'The Thermodynamics of Fluid Systems' (Clarendon: Oxford).
- Zener, C. (1948). 'Elasticity and Anelasticity in Metals' (Chicago Univ. Press).

### Appendix. Exact Rate Equations for Thermal Relaxation

The Néel (1949) approximation is conceptually unsatisfactory for problems of thermal relaxation in glasses where a heat pulse is applied and the subsequent behaviour of the temperature is monitored. An exact discussion within the confines of irreversible thermodynamics leads to results that are slightly different from those of Section 3. The working is as follows.

Suppose that a very short heat pulse is administered at time  $t = 0$ , the total heat given being  $Q$ . We wish to calculate the temperature of the system for times  $t > 0$ . The heat capacity  $C(t)$  of the system at time  $t$  is then formally defined in terms of  $\Delta T$ , the temperature rise, by

$$C(t) = Q/\Delta T(t). \quad (\text{A1})$$

For simplicity we consider the experiment to be conducted at zero strain. Then

$$(\partial T/\partial t)_e = (C_e^0)^{-1}(\partial U/\partial t)_e, \quad (\text{A2})$$

where  $C_e^0$  is the heat capacity of the matrix, i.e. the glass excluding internal degrees of freedom, and  $U$  is the internal energy of the matrix. This relation may be converted to a more useful form by employing the first law for the glass as a whole.

Let  $\tilde{U}$  be the total internal energy, so that we have

$$\tilde{U}(t) = U(t) + \sum_{\alpha} \int \Delta V^{(\alpha)}(q) N^{(\alpha)}(q, t) dq, \quad (\text{A3})$$

in the notation of Section 2. Consider the time derivative of this equation. On using the continuity equation (4), integrating by parts, specializing to steady-state conditions where the flux  $I^{(\alpha)}$  is constant in  $q$  space, and finally using equation (12), we have

$$d\tilde{U}/dt = dU/dt - \sum_{\alpha} \Delta V^{(\alpha)} dn^{(\alpha)}/dt. \quad (\text{A4})$$

However, the first law in the usual form

$$d\tilde{U} = dQ - V\mathbf{P}:\mathbf{de} \quad (\text{A5})$$

for closed systems can be applied, and hence

$$dU/dt = dQ/dt - V\mathbf{P}:(d\mathbf{e}/dt) + \sum_{\alpha} \Delta V^{(\alpha)} dn^{(\alpha)}/dt. \quad (\text{A6})$$

This form of the first law also leads to the result quoted in equation (5) of Section 2 for irreversible entropy production, since the fundamental Gibbs relation for a multicomponent system can be combined with equation (A6) to give

$$dS/dt = T^{-1}dQ/dt + T^{-1} \sum_{\alpha} \Delta \tilde{\mu}_{\alpha} dn^{(\alpha)}/dt. \quad (\text{A7})$$

The last term is the irreversible rate of entropy production (5) under steady-state conditions. However, only the form (A6) is required in this Appendix. It leads to

a usable form for the rate of change of temperature in the heat pulse experiment, namely

$$(\partial T/\partial t)_e = (C_e^0)^{-1} \sum_{\alpha} \Delta V^{(\alpha)} dn^{(\alpha)}/dt \quad (t > 0), \quad (\text{A8})$$

on noting that a  $dQ/dt$  term is absent, it being localized at  $t = 0$ . The initial temperature rise at  $t = 0$  is virtually instantaneous and equal to  $\delta Q/C_e^0$  where  $\delta Q$ , the heat input, is assumed small to produce a linear response.

The time derivatives of the populations  $n^{(\alpha)}$  are given by the rate equations (12) and (13). Let  $\delta n^{(\alpha)}(t)$  be the deviation from the initial equilibrium value which is given by equation (25) (with  $e = 0$ ), and  $\delta T(t)$  the rise in temperature. On linearizing the rate equations in these deviations, we obtain  $s+1$  coupled first-order linear differential equations:

$$\delta \dot{n}^{(\alpha)} + \delta n^{(\alpha)}/\tau^{(\alpha)} = -(\Delta C_e^{(\alpha)}/\tau^{(\alpha)} \Delta V^{(\alpha)})\delta T \quad (\alpha = 1, \dots, s), \quad (\text{A9a})$$

$$\delta \dot{T} = (C_e^0)^{-1} \sum_{\alpha} \Delta V^{(\alpha)} \delta \dot{n}^{(\alpha)}, \quad (\text{A9b})$$

with the boundary conditions  $\delta T(0) = \delta Q/C_e^0$  and  $\delta n^{(\alpha)}(0) = 0$ . In equations (A9a),

$$\Delta C_e^{(\alpha)} = N^{(\alpha)}(\Delta V^{(\alpha)} \Delta F^{(\alpha)}/4k_B T^2) \text{sech}^2(\Delta F^{(\alpha)}/2k_B T) \quad (\text{A10})$$

is the heat capacity of the active groups of type  $\alpha$ , and  $\tau^{(\alpha)}$  is the usual relaxation time of equation (16). Equation (A9b) can be integrated immediately and so  $\delta T$  can be eliminated from (A9a). This leaves us with  $s$  coupled first-order linear differential equations.

Fortunately, it is not necessary to have the exact solution, as the coupling terms are weak in practice. It is sufficient to obtain a perturbation expansion or iterative solution in which the leading term is the solution of  $s$  uncoupled equations, because the coupling parameter is  $\alpha$  which is normally smaller than unity. However, care must be taken to ensure that each term in the expansion has the right limiting value as  $t \rightarrow \infty$ , where the active groups have come to equilibrium at some new temperature. The limiting values are easily obtained from equations (A9a) and the integrated form of (A9b) by setting the time derivatives at zero. In this way we find that

$$\delta n^{(\alpha)}(\infty) = -\frac{\Delta C_e^{(\alpha)}}{\Delta V^{(\alpha)}} \frac{\delta Q}{C_e^0 + \Delta C_e}, \quad \delta T(\infty) = \frac{\delta Q}{C_e^0 + \Delta C_e}, \quad (\text{A11})$$

where

$$\Delta C_e = \sum_{\alpha} \Delta C_e^{(\alpha)} \quad (\text{A12})$$

is the total contribution of the active groups. These are just the values expected when the active groups have come to equilibrium.

The limiting values can be safeguarded in any approximate treatment by working not with equations (A9a) and (A9b) but with the corresponding homogeneous equations. These must be the corresponding equations in the deviations from *final* equilibrium. They will not be written down here. It will be sufficient to give the

solutions of zeroth order in the coupling constant  $\alpha$  for these new equations; these are

$$\begin{aligned}\delta n^{(\alpha)}(t) &= \frac{\delta Q}{C_e^0 + \Delta C_e} \frac{\Delta C^{(\alpha)}}{\Delta V^{(\alpha)}} \left\{ \exp\left(-\frac{t}{\tau^{(\alpha)}}\right) - 1 \right\}, \\ \delta T(t) &= \frac{\delta Q}{C_e^0 + \Delta C_e} \left\{ 1 + \frac{1}{C_e^0} \sum_{\alpha} \Delta C^{(\alpha)} \exp\left(-\frac{t}{\tau^{(\alpha)}}\right) \right\}.\end{aligned}\quad (\text{A13})$$

Although these forms are approximate, they have the right limiting values at  $t = 0$  and as  $t \rightarrow \infty$ . Higher order terms can be generated by solving the equations iteratively, and their effects are small for  $\alpha \ll 1$ . However, it is important to stress that the relaxation of temperature after an applied heat pulse is really a many-body problem if there are active groups of more than one kind. The number of 'bodies' is the number of different *kinds* of active groups.

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